Minimizing System Contamination Potential From Gas Handling

Studies reveal the best delivery methods for reactive gases used in advanced wafer processing.

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Recent increases in the use of reactive specialty gases in wafer processing prompted our study of traditional gas handling techniques: the goal was to retain gas-product integrity to a given process system, increase safety and increase mean time between failure of gas handling equipment.

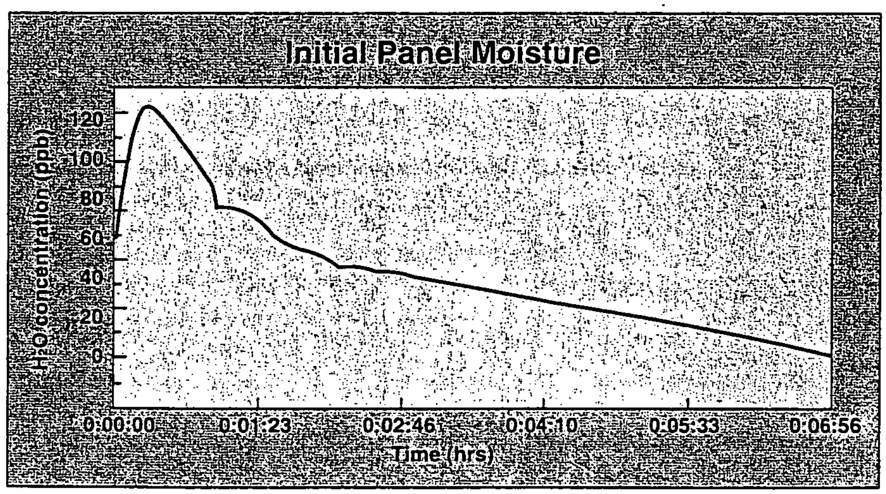
Atmospheric contaminants

Atmospheric contaminants that can compromise reactive gas delivery equipment are mainly water and oxygen. Infiltration of these gases can lead to corrosion of fluid containment subsystems and generation of particles.

In the case of the acid gases, such as HCl, HBr, HI and HF, researchers have found that even small amounts of water accelerate the corrosive attack of fluid containment materials, including accelerated corrosion of 316L stainless steel.[1,2] This corrosion most likely occurs from the formation of iron chlorides and iron oxychlorides. Oxidation and reduction corrosion processes generally occur cyclically until they consume the available water.

One should not assume that iron will be the only element involved in corrosion; metals, including nickel, chromium, molybdenum and other common metallic constituents of modern alloys can also be attacked.[3] Any acid halide gas can create metal halides and metal oxyhalides in the presence of water.

With SiH_4, B_2H_6, Si_2H_6 and PH_3, these gases react with oxygen or water to create oxides that can lead to particles in fluid containment systems.[4] These particles can plug orifices on mass flow controllers, pressure regulators and valves.



1. Gas panel "dry down" using 4.8 slpm dry nitrogen.

Others have studied the behavior of WF_6 with 316L stainless steel; this gas can react with the metal oxides of stainless steel without water.[5-6] In this unique case, a passive fluoride film on the stainless steel can prevent the interaction. However the fluoride film is not stable in the presence of water; the fluoride layer degrades by hydrolyzing quickly.[7] Therefore it is necessary to prevent exposure of standard fluorine passivated materials to water.

The challenge for designing and managing process gas handling equipment, therefore, is to remove these contaminants during equipment manufacturing start-up, cylinder changes and maintenance procedures, and otherwise prevent the intrusion of water and oxygen into the gas containment system.

Consider, for example, a "dry down" curve (Fig. 1) for a six-valve process gas panel: the integrated area under the curve is moisture to remove from the panel if an inadvertent, brief exposure to the atmosphere occurs.

Cylinder changes

Cylinder changes most often jeopardize the integrity of the gas handling system. Most process engineers are familiar with the procedure of purging the "pigtail" section of a process gas panel with an inert gas and the need to prevent back diffusion of atmospheric gases during cylinder change.

Research has shown that beyond ten cycle-purges (one cycle consists of evacuation and pressurization) there is no significant additional removal of process gas.[8] However, if the evacu-

ation side of the purge does not use sufficient vacuum, both process and atmospheric gas contaminants physisorb to the inside walls of the pigtail and will not be adequately removed. Gas panels commonly achieve vacuum evacuation with either a vacuum venturi or mechanical vacuum pump:

- A **vacuum venturi** typically achieves a 200 Torr vacuum, four orders of magnitude poorer than the vacuum obtained with a rotary vane or claw type vacuum pump. At this vacuum, it does not adequately remove reactive or atmospheric gases from dead spaces, nor those that physisorb to inside walls of a gas delivery system. A vacuum venturi can also back diffuse water vapor into a gas panel because its exhaust is usually back diffuse to the exhaust of a mechanical pump, it does not make it to the critical low pressure side.

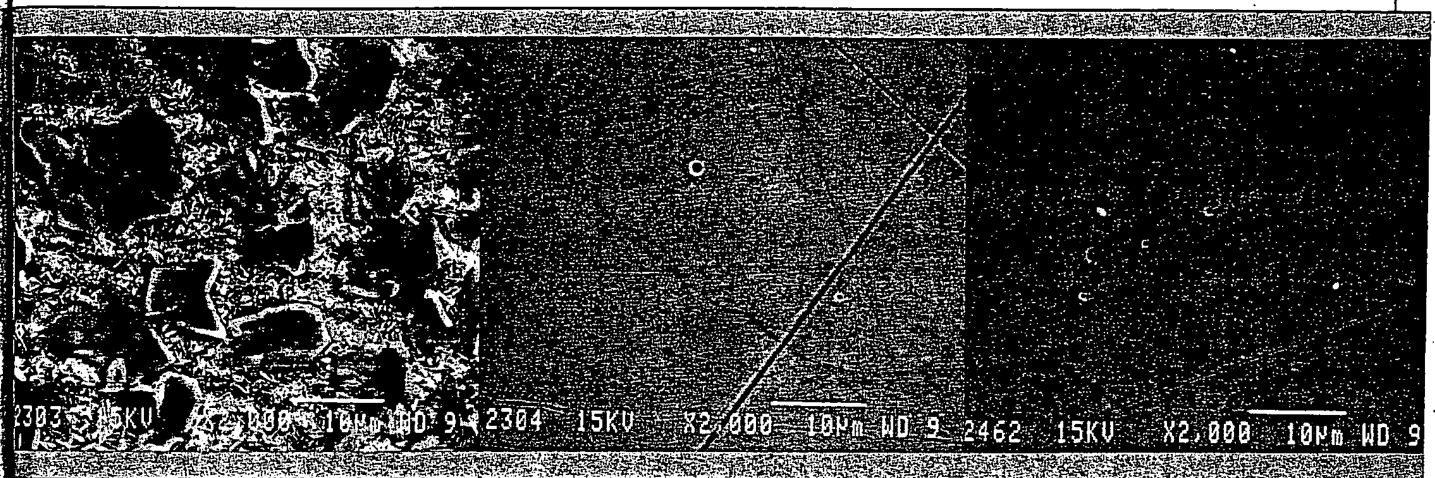
Research has shown that diffusion of atmospheric gases into an open tube can be prevented with an inert gas velocity equal to or greater than 78 ft/sec exiting the tube.[11] Applying this to a gas delivery system means the open end of a pigtail must have an orifice that allows a pressure drop during cylinder changes that keeps the purging inert gas velocity at 78 ft/sec; the orifice must also allow adequate flow of *process gas* during normal process gas panel operation. The orifice only serves the purpose of accelerating the gas flow out of the pigtail during cylinder changes reducing the consumption of purge gas.

cylinder and connect a new cylinder. The pigtail purge gas was research-grade nitrogen. The pigtail had a 0.090 in. orifice with a choked flow at a 25 psig. The pressure drop of nitrogen to atmosphere was 45 psi.

Overall, the ten purge cycles meant we were simulating a complete cylinder change procedure of about 25 min.

Through 25 simulated cylinder changes, we found no evidence of tungsten oxide or tungstic acids on the interior of the pigtail (see Table 1).

In another series of tests using a vacuum venturi, we brought the pigtail down to 200 Torr in 2 min and then pressurized it to 60 psig for 5 sec. We completed a total of 15 simulated cylinder changes using the vacuum venturi for the purge-cycle. Interestingly, venturi equipped process panels typically call for 50 to 60 cycle-purges; this corresponds to a cylinder "change out" time of about four hours.



2. Tests with vacuum venturi evacuation show a) crystallites or areas attacked by wet HBr, while tests with vacuum pump evacuation show b) a stainless steel sample similar to the control sample c).

piped to atmosphere or an aqueous based scrubber system; some have traced recent field analyses of failures in HBr and HCl gas process panels to this phenomenon. Back diffusion is a cumulative effect that does not manifest itself until months of operation.

- With a **mechanical vacuum pump**, the 100 milli-Torr pressure regime is at the transition between free molecular flow (>1.0 Kn) and viscous flow (<0.1 Kn). For quarter-inch stainless steel tubing the Knudsen number (Kn) at 20°C is 0.07 Kn and 0.019 Kn for 1 in. Obviously, you must apply these pumps knowledgeably: oil pumps must be compatible with halide gases, backstreaming and oil suck back must be eliminated,[9,10] and proper contaminant traps must be used. While water can

Cycle-purge testing

We used WF_6 to compare the efficiencies of a mechanical vacuum pump and a vacuum venturi in a process gas panel. First, we performed ten cycle-purges to remove WF_6 from the pigtail prior to removing the empty cylinder: using a mechanical vacuum pump for evacuating the pigtail, the ten cycle purges involved pumping to 110 milli-Torr in approximately 60 sec followed by pressurization to 60 psig in approximately 5 sec. Research has shown that this type of purge cycling is the most effective method to remove residual contamination in a section of tubing.[8]

To simulate the cylinder change, we left the cylinder and pigtail connections open for two minutes to approximate the time necessary to remove an empty

With these tests using the vacuum venturi, we found noticeable deposits of tungsten oxides and tungstic acids after only ten simulated cylinder changes (see Table 1).

HBr testing

To test the procedures for changing a cylinder of HBr, we first used a molecular drag pump, capable of a 1 × 10^{-7} Torr base vacuum, to evacuate a 2 in. diameter tube containing samples of EP316L stainless steel. We held the tube under vacuum for 18 hours before exposing it to HBr. A similar tube with

Table 1. Data from Cycle-purge Testing

Cylinder change #	Observation after vacuum venturi base pressure 110 Torr*	Observation after mechanical vacuum base pressure 0.1 Torr**	Comments
1-4	No WO_xF_y deposits	No WO_xF_y deposits	Face metal seal discolored
4-25	WO_xF_y deposits in pigtail	No WO_xF_y deposits	Boroscope used to observe interior tubing deposits

* Vacuum venturi — cycle purge parameters: 10 cycles, 5 minute evacuation, 60 psig purge through orifice.
**Mechanical vacuum — cycle purge parameters: 10 cycles, 1.3 minute evacuation, 60 psig purge through orifice.

stainless steel samples was evacuated to 200 Torr via a vacuum venturi and cycle-purged with purified nitrogen before exposure to HBr.

We then analyzed stainless steel samples from each test using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) to determine surface changes:

- SEM micrographs clearly show that the sample from the vacuum venturi test (Fig. 2a) had been "attacked" by the HBr; the sample from the molecular drag pump test (Fig. 2b), with its lower base pressure, looked much like our control stainless steel sample (Fig. 2c).
- EDX analysis and AES depth profiles of the HBr samples showed incorporation of bromine in the samples from the venturi test.

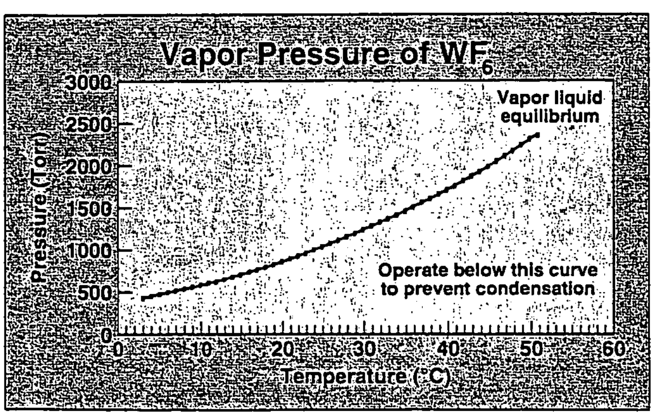
The better techniques for cycle purging that we identified in these tests, specifically those for outgas monitoring and pigtail trickle purge, have been incorporated in an HBr production facility at Air Products and Chemicals. Using these methods for minimizing atmospheric contamination, our fill facility provides virtually contamination free product. Additionally, to further minimize system related contamination, this new system incorporates on-line process analysis of the HBr during fill procedures to guarantee gas purity in the cylinder. This procedure has given zero defect rates for gas cylinder valve corrosion.

Fluid dynamics of gas delivery

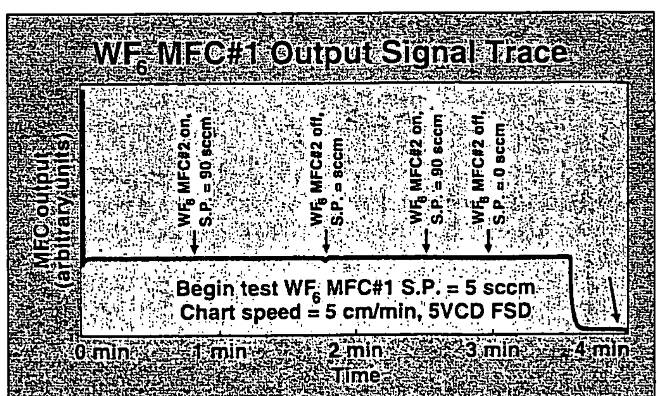
Low vapor pressure gases, such as BCl_3, WF_6, SiH_2Cl_2, contained as liquids under their own vapor pressure, present particular problems in delivery of gas to wafer processing systems. All of these gases have similar vapor pressure curves (see Fig. 3).[12] The foremost problem is to prevent condensation of the gas in delivery lines. Here, one must design a process gas panel to keep gas conditions in the process tubing below the saturation point of the gas, using one of three possible methods:

- Heat the gas cylinder and supply lines — This type of installation requires a bottle heating jacket and tubing heaters that keep the bottle at about 70°F and a positive temperature gradient in the lines to the process tool. In some applications, this method may accelerate the corrosion of the fluid containment system or cause premature decomposition of the process gas.
- Chill the gas cylinder — Special cylinder chillers cool the gas cylinder below the ambient temperature, keeping it below the coldest temperature that supply lines attain going to the wafer processing system. Also, some engineers prefer to provide a positive temperature gradient to the process tool.
- Lower gas delivery pressure — Using an absolute pressure regulator, capable of handling the low vapor pressures of the gas in question, maintains the delivery pressure of the process gas at a point on the vapor pressure curve of the gas that is below the gas saturation point of the lowest temperature attained by process lines. In these applications, equipment designers place the regulator as close to the cylinder as possible. In addition, in most applications for these types of gases, the process tool runs at low pressure, therefore allowing subatmospheric pressure delivery of the process gas.

Typical process piping runs for most process gases use quarter-inch tubing. Flow rates are usually low enough that most processes run at laminar flow. The fluid dynamics of low vapor pressure gases through tubing and flow control



3. *Points indicate upper bound operating conditions for prevention of gas condensation.*



4. *Resulting MFC response to sudden changes in flow rate through WF_6 gas manifold.*

Flow Regimes

Flow rates are typically low enough that most processes are run at laminar flow. Flow is considered laminar if the Reynold's number (Re) is below 2000.[13] The Re number is defined for tubing by

$$Re = \frac{4F_{sccm}\rho}{60\pi D\mu}$$

where
F_{sccm} = flow rate in cm³/min at stp,
ρ = gas density in g/sm³,
D = internal tube diameter in cm and
μ = gas viscosity in g/cm-sec.

For example, with a WF_6 flow at 500 sccm the Reynold's number is about 1200 and therefore the flow is laminar. Like most of the gases mentioned in this article, this is an extremely large Reynold's number: it is from the high density of gaseous WF_6. Therefore, in this flow regime, some engineers estimate flow rates by the Hagen-Poiseuille equation[14]

$$F_{sccm} = \frac{79992\Delta p_s g_c D^2}{32\Delta L\mu}\pi(D/2)^2\frac{P_{exit}}{760}$$

where (in addition to previous definitions)
Δp_s = pressure drop in Torr,
g_c = gravitional constant (1 for cgs),
ΔL = tubing run length in cm and
p_{exit} = pressure at end of tube in Torr.

This equation predicts a maximum flow for WF_6 of 6.6 SLPM at a pressure drop of 200 Torr and exit pressure of 80 Torr in a 350 ft quarter-inch diameter (OD), 0.040 in. thick tube at 25°C. Alternately, when dealing with compressible gases with large changes in gas properties the equation for compressible isothermal frictional flow should be used[13]

$$F_{sccm} = \frac{1}{\rho}\sqrt{\frac{\frac{M.W.(p_a^2 - p_b^2)1332^2}{2RT}}{1n\frac{p_a}{p_b} + \frac{f\Delta 1}{D}}}\pi\left(\frac{D}{2}\right)^2$$

where (in addition to previous definitions)
R = gas constant 8.3071 x 10⁷ g-cm-cc/cm²sec²gmole K,
p_a = inlet pressure in Torr,
p_b = outlet pressure in Torr,
T = ambient temperature Kelvin,
Δl = length of pipe in cm and
f = fanning friction factor.

Tables showing the fanning friction factor as a function of Reynold's number are available in several fluid dynamic texts (see for example reference 13). This equation with a fanning friction factor of zero predicts a volumetric flow rate of 1.1 slpm in contrast to the 6.6 slpm predicted for the same conditions by Poiseuille's equation. This result shows that the equation for compressible isothermal flow[3] is useful to determine the maximum delivery length for these gases (Figure 4 shows the measured flow rate for these conditions and confirms the equation is an accurate description of the expected flow).

The largest resistance to flow arises from the valves and pressure control equipment used in gas panels, valve manifolds and process gas jungles. Here, we can find the flow rate of the gas by combining the equation of compressible flow for a gas and the specific valve conditions such that

$$F_{sccm} = 8794.3C_v\sqrt{\frac{\frac{p_a^2 - p_b^2}{\rho}}{1.29\times 10^3}T}$$

where (in addition to previous definitions)
C_v = flow coefficient for flow element
ρ = density of gas in g/cc and
T = temperature in Rankine.

For a WF_6 flow rate of 500 sccm, the pressure drop would be 5 Torr across a valve having a C_v of 0.08 and inlet pressure of 280 Torr. While this is not a substantial pressure drop, when a number of flow components is installed, the cumulative effects of these components can lead to substantial pressure drops at low delivery pressures. □

components shows that significant flow rates can be achieved over relatively long distances if the flow path remains unobstructed (see "Flow Regimes," which appears with this article).

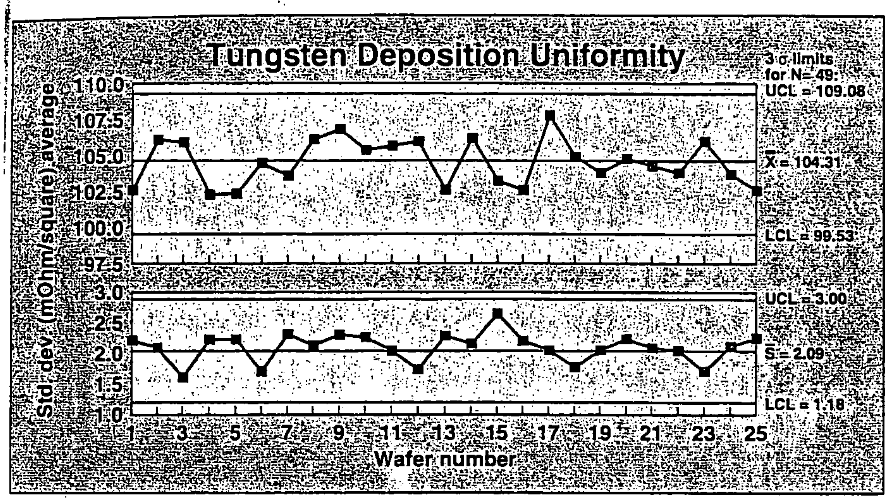
With corrosive gases, problems result when byproducts, from the reaction of a process gas with the atmosphere or incompatible materials, plug gas control components. If you use the gas handling techniques outlined above, you will not have any atmospheric contamination in the process lines. On the other hand, flow control components and their materials of construction must be compatible with the process gas. For example WF_6 swells Teflon, which in the case of Teflon valve seats significantly reduces the flow coefficient of the valve. This can cause excessively large pressure drops, leading to flow restrictions or in a worse case, cause Joule-Thompson cooling of the gas — it condenses to a liquid upon exiting the valve.[2]

For consistent, reliable flow to a process tool, it is imperative to use the largest flow coefficient available for the type of valve or regulator chosen. It is also beneficial to reduce the amount of polymeric material in the flow path. Polymers tend to have very porous morphologies that contain large quantities of adsorbed moisture capable of reacting with process gases to form particles or swell the polymer.[14]

Putting it all together

As semiconductor manufacturers try to reduce the total cost of their facilities, "gas pad" engineers are examining methods of manifolding several reactors to one process gas source. While this approach is not problematic for high pressure gases, it presents unique problems for low pressure gases.

Consider, for example, manifolding two or more independently operated mass flow controllers (MFCs): sudden increases in flow when one MFC is operating and another comes on-line decreases pressure in the delivery system as demonstrated by fluid dynamic analysis (see "Flow Regimes"). This causes the MFC to lose its ability to maintain a stable process gas flow; accordingly, system designers must place a flow component that maintains a constant pressure immediately upstream to the MFC. An additional absolute pressure regulator at the inlet of each MFC will maintain a constant pressure at the inlet of the MFC and prevent flow oscil-



5. Control plots of as deposited tungsten sheet resistance uniformity for a sequence of wafers.

lations when other process MFCs demand flow.

Air Products has built a WF_6 delivery system like this that supports four MFCs from one process gas line. This system features:
- a gas cabinet incorporating a rotary vane vacuum pump for cylinder change cycle purging,
- subatmospheric, pressure regulated, high purity coaxial piping,
- VCR fittings throughout with a metal seal CGA DISS cylinder fitting,
- low volume manometers and strain gauge pressure transducers, and
- nickel media particle filters.

In preparation for the actual process gas, the system was baked at 60°C and purged with ultrahigh purity nitrogen for 24 hours before fluorine passivation of the system; here, we returned the line to ambient temperature, evacuated to less than 100 milli-Torr and backfilled with a 10% fluorine-in-nitrogen mixture that sat in the tubing for 36 hours. Finally, we pumped the fluorine-nitrogen from the process lines and cycle purged the system before introducing WF_6.

Data (Fig. 4) clearly show that the MFCs in this system do not interfere with one another; they provide consistent flow even when another MFC comes on. Studies showing repeatability, film purity, uniformity and other process parameters indicate that the system is performing as designed. SIMS data show the high purity of deposited films from WF_6 process gas delivered through this system; extremely small amounts of iron and nickel (we did not detect chromium in the analysis) show no contribution of the stainless steel used in the delivery system. Figure 5 shows deposition uniformity results as measured by sheet resistance for consecutive runs.

Air Products' WF_6 gas delivery system has given 100% uptime since coming on-line at Motorola's MOS-11 facility more than one year ago. The system's components have not shown any signs of failure or even drift in their processing characteristics. We believe, also, that we've minimized system degradation by using an oversized cylinder system; the system requires roughly two cylinder changes per year. Minimizing cylinder changes also minimizes atmospheric contamination.

Acknowledgments

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